10-1993

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Abstract
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Keywords
Ames Laboratory, spectroscopy, cerium, monolayer suboxide formation

Comments
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Photoemission study of Ce-catalyzed oxidation of W(110) and W(111)

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(Received 28 December 1992)

Different catalytic oxidation effects of Ce on W(110) and W(111) were observed with photoemission spectroscopy. On Ce-covered W(110), the top W layer is quickly oxidized to a surface monoxide at room temperature. Oxidation is almost halted after the completion of one monolayer of WO. On Ce/W(111), instead of WO, WO_3 grows on the surface under the same conditions. The monolayer suboxide formation found on Ce/W(110) and Ce/Ta(110) (as reported earlier) is a direct consequence of the most densely packed structure of the bcc (110) surfaces. The more effective oxidation promotion on the W(111) surface is attributed to its open structure. The mechanism of Ce-catalyzed oxidation is further tested in this study.

I. INTRODUCTION

The oxidation promotion effect of rare-earth overlayers on a variety of metal and semiconductor substrates has been observed in the past.[1–8] Some of the systems studied, e.g., (Ce, Sm)/Si (Refs. 2, 3, and 8) and (Ce, Pr)/Al (Refs. 4 and 5) are reactive in terms of interface mixing and alloying. No interdiffusion was found in interfaces with Nb,[1] Ta,[4,6] or W (Ref. 9) as substrates, so they are more suitable for the study of catalytic oxidation. It was proposed that the existence of two Ce oxides, namely Ce_2O_3 and CeO_2, allowed the conversion of adsorbed oxygen to oxygen ions, thus enhancing the rate of substrate oxygen incorporation.[1] This mechanism is supported by the observation that only rare earths with two oxidation states, such as Ce, Pr, and Tb, are catalysts.[1] In the oxidation of Ce/Nb, Nb_2O_5 forms quickly beneath a Ce layer. No Nb suboxides were observed by x-ray photoemission spectroscopy (XPS), which is relatively bulk-sensitive. Ronay and Norlander[10] considered that the lack of Nb suboxide formation might also be related to rapid Nb oxidation in Ce/Nb, since their calculation shows that the NbO layer usually forming in the oxidation of bare Nb is a good barrier to further oxygen incorporation due to the higher embedding energy for the oxygen atoms.

Recently we studied the catalytic oxidation of Ce/Ta(110) with surface-sensitive soft-x-ray photoemission spectroscopy.[6] The Ta substrate has two oxidation stages. First the top Ta layer is oxidized to a suboxide with a well-defined $4f$ core-level shift of 0.95 eV (with respect to the bulk). Subsequently Ta_2O_5 forms. Due to the lack of precise values of core-level shifts for Ta suboxides, the Ta surface suboxide formed in the oxidation of Ce/Ta(110) could only be described as TaO_χ, $0.5 \leq \chi \leq 1$. Other studies of rare-earth/metal oxidation used polycrystalline samples as substrates. A substrate suboxide was either not observed (especially in bulk-sensitive XPS studies), or was not well defined in the spectra. To understand the role of substrate suboxide formation in the catalytic process, we chose to study W, the next element to Ta. W has the same bcc structure as Ta. Also like Ta, it does not alloy with Ce, as concluded in Ref. 11. In this paper we present results on the oxidation of Ce/W(110) and compare them with the earlier study on Ce/Ta(110). Experiments on the oxidation of Ce/W(111) clarify the role of the monolayer suboxide formation on the (110) surfaces of W and Ta, and demonstrate the significance of substrate surface structure in catalytic oxidation. The effects of substrate and oxide structures on oxide formation have been studied theoretically by Nordlander and Ronay[12] for $3d$ transition metals and their oxides. Oxygen diffusion is important for several models of oxide growth and the activation energy for diffusion was shown to depend on substrate and oxide structure. In addition, relaxation about the diffusing oxygen, modeled with an elastic continuum, was shown to be important for reducing the energy barrier for diffusion.

The oxidation of W(110) has been studied extensively,[14–17] partially due to the existence of ordered adsorption structures. At room temperature, oxidation up to 3–4 L [1 L (langmuir) $\equiv$ 10^{-6} Torr sec] yields a $p(2 \times 1)$ structure on the (110) surface. The oxygen binding sites on the $p(2 \times 1)$ surface have been determined by Van Hove and Tong.[16] Their calculation, compared with low-energy electron-diffraction (LEED) data, indicates that oxygen atoms occupy the threefold-coordinated binding sites. Photoemission studies show that the W surface $4f$ core levels shift about 0.6 eV to higher binding energies (or +0.3 eV relative to the bulk) at this oxygen coverage. After the completion of the $p(2\times1)$ phase, oxygen uptake is slowed quickly. After heavy O_2 exposure, the $4f$ core-level spectrum shows a new oxide at a binding energy 0.7 eV higher than that of the bulk.

Unlike W(110), oxidation of the W(111) surface does not yield an ordered adsorption structure.[18–20] Oxygen adsorbate sites were studied by measurements of the angular distribution of electron stimulated desorbed ions (ESDIAD).[19,20] In all adsorption models proposed,

the W surface atom sites are considered to be undisturbed. Photoemission measurements[21] show broad core-level shifts 0.4–0.5 eV higher than the bulk after ~2 L O_2, reflecting the disordered adsorption as well as the larger charge transfer on the open (111) surface. A surface oxide with an ~0.7-eV chemical shift (relative to the bulk) can be obtained by repeated heating of the sample in 10^{-6} Torr of oxygen.[22] Extensive reviews of W surface oxidation above room temperature can be found in Ref. 23.

The Ce/W(110) interface structure has been investigated by measurements of W 4*f* surface core-level shifts, Ce 4*f* resonance spectra, and LEED patterns. There is no interdiffusion at the Ce/W interface. The catalytic oxidation is independent of Ce coverage as described later. Detailed results on the adsorption patterns as a function of Ce coverage and the corresponding electronic structure will be reported elsewhere.[9]

II. EXPERIMENT

The photoemission experiments were conducted at the Synchrotron Radiation Center, University of Wisconsin-Madison, using the Ames/Montana beamline.[13] Photoelectron spectra were taken with a hemispherical electron-energy analyzer (VSW HA50), used at normal emission with an angle resolution of ±1°. The base pressure in the vacuum chamber was 5×10^{-11} Torr. The W(110) and W(111) crystals were thin disks 5 mm in diameter. Their orientations were checked to be accurate within 1° by Laue x-ray diffraction. Each sample was clean after about 10 h of cumulative anneals at ~ 2300 °C. Electron beam bombardment was employed to reach the high temperature, which was monitored by an optical pyrometer. Before each experiment, the W crystal was flashed to ≥ 2300 °C to remove any residual contamination from the surface. The sample cleanliness was verified by observation of sharp and stable LEED patterns, and the surface 4*f* core-level line shape. A piece of high-purity Ce metal was melted in a W basket, and was degassed thoroughly prior to evaporation. The Ce thickness was monitored by a quartz oscillator.

III. RESULTS

A. W(110)

We oxidized a W(110) surface covered with 4.7 Å of Ce at room temperature. The O_2 pressure was 1×10^{-8} Torr. Figure 1 shows W 4*f* spectra taken at normal emission. The spectra extend a few eV higher than the W 4*f* spin-orbit split peaks, so that all possible W oxides can be observed. The W $5p_{3/2}$ level is located in the extended region. We choose $h\nu = 110$ eV so that this peak is much weaker than the 4*f* levels. The energy resolution for all W 4*f* spectra in this paper is 0.26 eV. Clean W(110) has a surface 4*f* core-level shift (SCS) toward lower binding energy. Analysis of W(110) 4*f* spectra taken with higher resolution (0.14 eV) shows a −316

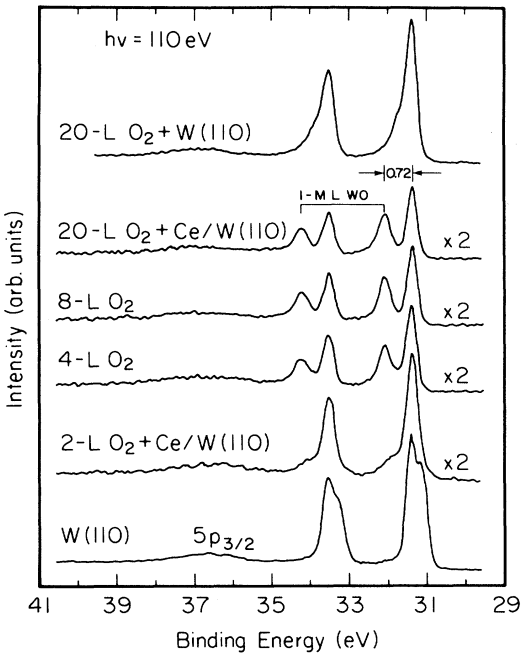

FIG. 1. W 4*f* spectra after 4.7-Å Ce/W(110) was exposed to various amounts of oxygen.

± 4 meV SCS,[9] in good agreement with other studies. After the Ce-covered W(110) surface is exposed to 4 L of O_2, a new well-defined doublet emerges at 0.72 eV higher binding energy than the bulk levels. After 8 L of O_2, the growth of the new oxide is almost completed. Further oxygen exposure up to 20 L does not produce any other oxide at higher binding energies, and the W oxidation is virtually halted. The relative intensity of the new peaks compared with the bulk peaks indicates the top W layer is uniformly oxidized, whereas atoms beneath are not affected. The W surface oxidation rate depends negligibly on the thickness of the Ce layer; the same W surface oxidation for these exposures was observed on W(110) with a Ce coverage as low as 0.7 Å. The oxygen mobility through the Ce oxide is evidently high.

For purposes of comparison, the oxidation was repeated on clean W(110) under the exact same conditions. The top curve in Fig. 1 shows that after 20 L of O_2 exposure, the surface components appear as shoulders at the higher binding energy side of the bulk peaks. To achieve surface oxidation close to that with Ce, one has to dose with large amounts of oxygen and/or anneal the sample in oxygen. Therefore, the oxidation of bare W(110) is inefficient under present conditions. Ce greatly promotes the oxidation of the first layer of W(110) at room temperature, but falls short of producing bulk substrate oxidation.

To determine the W suboxide formed on Ce/W(110), we may compare its chemical shift with those of other W oxides. Table I lists measured 4*f* core-level shifts in a few W oxides. There are at least two well-known W suboxide states: the $p(2\times1)$-O/W(110) surface oxide, and WO_2, a bulk metallic suboxide. Their 4*f* chemical shifts are 0.3

TABLE I. W $4f$ chemical shifts (in eV relative to the bulk) for W oxides. The 1+ state is assigned to the $p(2 \times 1)$-O/W(110) surface oxide. Some values are averages of data provided in the references.

W Oxides	0	1+	2+	4+	5+	6+
Ref. 17		0.3				
Ref. 24			0.71	1.6		4.3
Ref. 25				1.5	2.7	4.5
Ce/W(110)+O_2			0.72			
Ce/W(111)+O_2						4.1
W(110)	−0.32					
W(111)	−0.45					

eV and ~ 1.6 eV, respectively. A surface oxide with a 0.71 eV shift was assigned to W^{2+}.[24] These results convince us that the W suboxide formed on Ce/W(110) with a 0.72 eV shift should be assigned to a surface monoxide WO. We acknowledge that this assignment simply implies a one-to-one tungsten-oxygen stoichiometric ratio for the top atoms on W(110). We do not attempt to relate this surface oxide to a bulk monoxide structure, as solid WO is not well known.[26]

The formation of 1 monolayer (ML) of substrate suboxide on Ce/W(110) is strikingly similar to the case of Ce/Ta(110).[6] In both cases the suboxides form on the top layer of the transition metal surface after 4 − 8 L O_2. Their sharp $4f$ line shapes are also very much alike. The overwhelming similarity suggests an identical stoichiometry for these two suboxides. The TaO_x found in the initial oxidation of Ce/Ta(110) should be close to TaO. The minor difference in their core-level shifts is not unusual. In fact, bulk WO_3 has a 4.5 eV chemical shift in the $4f$ core levels, whereas Ta_2O_5 has a larger value of 5.1 eV.

Unlike Ce/Ta(110), however, the oxidation of Ce/W(110) is almost halted after the completion of WO on the first layer. The difference can be understood by considering the slow oxidation of pure W itself. It has been shown that bare W(110) is much more resistant to oxygen than Ta(110). Initial oxidation of Ta(110) up to 15 L produces surface suboxides with 1−2.5 eV shifts (relative to the bulk core levels).[6] Similar oxygen exposure on W(110) only produces an ~0.3-eV shift (relative to the bulk) for the top layer. W has the highest cohesive energy of the $5d$ transition metals. Its oxide WO_3 has a lower Gibbs free energy of formation (183 kcal/mol) than Ta_2O_5 (228 kcal per mole of Ta^{5+}).[27] Another factor, probably of more importance, is that W is a hard metal with a much larger bulk modulus (3.23×10^{11} N/m^2) than Ta (2.00×10^{11} N/m^2).[28] The rigidity of the W lattice may impede oxygen penetration at room temperature or lower.[10,12]

B. W(111)

So far we have observed the formation of a Ce-promoted transition-metal monoxide on both Ta(110) and W(110). Its role in the catalytic process, however, is still unclear. A rather important unanswered question is whether the suboxide formation is an essential step in the catalytic oxidation, or is it only so on the bcc (110) surface. Therefore a comparative study on another surface, such as (100) or (111), may provide the answer. We prefer W(111) over W(100), simply because the (100) surface shows relaxation at room temperature and a $c(2 \times 2)$ reconstruction at low temperature.[29] The W $4f$ spectrum taken from a clean (111) surface is shown as the bottom curve in Fig. 2. It is well known that due to the reduced coordination number, the W(111) surface has a large SCS (−0.45 eV) for the top-layer atoms. The first underlayer is not well covered by the topmost surface atoms, and a smaller SCS has been found. While no SCS was found for deeper atoms by Wertheim and co-workers,[30,31] another group[22] reached the totally different conclusion that there is significant SCS for the second underlayer. The existence of multiple SCS on W(111) complicates the core-level structure with Ce adsorption. Here we will concentrate on the catalytic oxidation of the W(111) surface, as large chemical shifts can be unambiguously identified, and simply point out that, similar to Ce/W(110), we observed W(111) surface core-level shifts to lower binding energies upon Ce adsorption.

3 Å of Ce was evaporated on clean W(111). Again the Ce-covered surface was oxidized at 1×10^{-8} Torr O_2. As shown in Fig. 2, after 4 L of O_2 exposure, the $4f$ spectrum reveals a new W oxide with a chemical shift of 4.1 eV, which should be assigned to WO_3 (see Table I). The much broadened lines in the oxide are characteristic of an insulating oxide.[24] It is interesting to note that WO_3 is the main oxide product, and only a small amount of suboxide can be seen as the shoulders on the higher binding

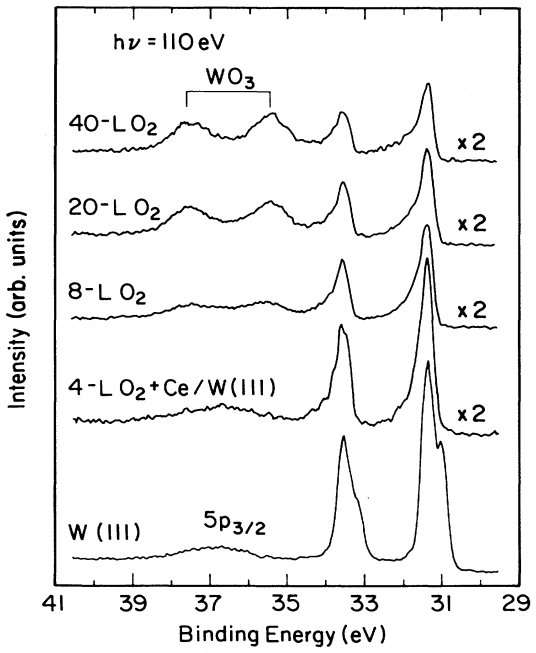

FIG. 2. W $4f$ spectra after 3.0-Å Ce/W(111) was exposed to oxygen.

energy side of the bulk levels. The well-developed surface monoxide found on Ce/W(110) is absent on Ce/W(111).

The much heavier oxidation found on Ce/W(111) is comprehensible in terms of the structure of different surfaces. The (110) surface is the most densely-packed one for a bcc solid, which should give rise to a higher barrier to oxygen penetration than surfaces of other orientations.[12] The geometry also allows for the formation of a stable monoxide on the first layer, one likely to be ordered as indicated by its sharp core-level line shape. Ronay and Nordlander reported that the formation of NbO on Nb(110) significantly increases the potential barrier for further oxygen incorporation.[10] The 1 ML of WO formed on Ce/W(110) may also act like an oxidation barrier,[12] for there is no further oxidation observed. On the W(111) surface, the atoms in the top layer are more open to the O_2 side, so they are more vulnerable to surface chemical reaction. The cohesive energy of surface atoms, smaller than that of the bulk atoms due to reduced bonding, is related to the number of bonds and their distances (pair-bonding model).[32] The top atoms on W(111) have only four nearest neighbors (NN) and three next-nearest neighbors (NNN). The reduced number of neighbor atoms on the W(111) surface should correspond to a smaller surface-atom cohesive energy than on the (110) surface, which has six NN's and four NNN's. Thus it is easier to dislodge the top atoms on (111) surfaces by chemical reaction such as oxidation. When the top atoms are oxidized to WO_3 and presumably removed from their original sites, the second layer may subsequently become vulnerable to oxidation, i.e., there may be no protective layer on the surface. From the relative intensity of the W and WO_3 $4f$ peaks (Fig. 2), we estimate that about two W layers have been oxidized after 40 L O_2. Therefore it is concluded that oxidation on the (111) surface is much more effective due to its open structure.

C. Ce + O_2

The Ce layer and its oxide states are studied with the $4d \rightarrow 4f$ absorption spectra[33] shown in Fig. 3. The $4d \rightarrow 4f$ transition in a lanthanide has a very rich absorption structure due to the strong electrostatic and exchange interactions involving the spatially overlapping $4d$ hole and $4f$ electron(s). Some sharp peaks can be observed well below the autoionization threshold. The fine structure is very sensitive to the $4f$ occupancy. The $4f$ level in CeO_2 is nominally empty ($4f^0$), so its spectrum is like that of La, very different from that of Ce_2O_3 and Ce (both formally have a $4f^1$ configuration). The proposed mechanism of catalytic oxidation[1] is that changes between the trivalent ($4f^1$) and tetravalent ($4f^0$) oxide states help convert oxygen to ions and promote substrate oxidation. On Ce/W(110), substrate oxidation is almost completed after 8–20 L of O_2. Consequently, the oxygen-ion-rich CeO_2 will accumulate in the Ce layer. This can be seen in the fine structure, where a peak at 108 eV characteristic of CeO_2 grows (curves B and C). At 20 L of O_2, it is already larger than any $4f^1$-related feature. The same measurement during the oxidation of Ce/Ta(110) (with similar Ce coverage) yields a much smaller relative intensity for the 108-eV peak even at a higher O_2 exposure (40 L),[6] since the Ta substrate was still being oxidized. The relatively fast accumulation of CeO_2 in the oxidation of Ce/W(110) is consistent with the suggested catalytic mechanism.

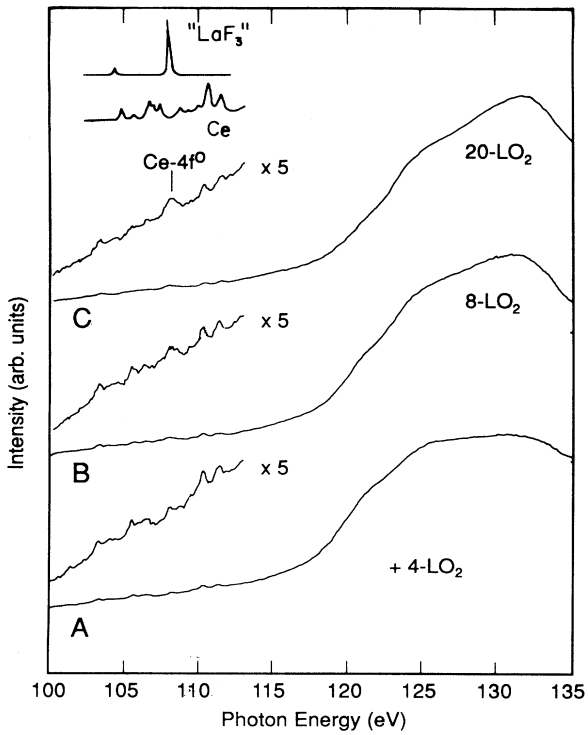

FIG. 3. Ce $4d \rightarrow 4f$ absorption spectra taken during the oxidation of Ce/W(110). The inset shows spectra for bulk Ce, nominally Ce^{+3}, and LaF_3, the latter shifted 6 eV to higher energy to mimic Ce^{4+}.

IV. SUMMARY

The experiments on the oxidation of Ce/W(110) and Ce/W(111) clearly demonstrate that substrate orientation plays a significant role in catalytic oxidation. The Ce layer can be viewed as the oxygen activator and reservoir. The catalytic effect strongly depends on the substrate material as well as its specific surface structure. The surface orientation dependence in oxidation is probably highlighted in the presence of a catalytic overlayer, since other rate-limiting factors, such as surface oxygen molecule dissociation and oxygen sticking probability, are largely diminished. Comparative oxidation studies of surfaces of various orientations with and without a catalytic overlayer may complementarily enrich our understanding of the catalytic oxidation and the general surface oxidation itself. Experiments on polycrystalline samples may yield a mixed picture contributed by do-

mains of various surface orientations.

We have shown that Ce promotes oxidation of both (110) and (111) surfaces of W, but the effect is much stronger for the open (111) surface. Surface oxide products are different due to the surface structure. The monolayer substrate monoxide found on Ce/W(110) and Ce/Ta(110) is due to the most densely-packed structure of the bcc (110) surfaces. Observation of Ce^{4+} and Ce^{3+} states agrees with expectations from the proposed catalytic mechanism.

ACKNOWLEDGMENTS

We would like to thank Dr. R. S. Hansen and Dr. P. A. Thiel for providing the W crystals, and B. J. Beaudry for the supply of Ce. The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-ENG-82. The Synchrotron Radiation Center is operated by the University of Wisconsin under National Science Foundation Contract No. DMR-86-01349.

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